

***Synthesis and Characterization of Oxovanadium
Complex Incorporating Dimethyl Terephthalate Moiety***

A Dissertation

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CERTIFICATE

This is to certify that the dissertation entitled “*Synthesis and Characterization of Oxovanadium Complex Incorporating Dimethyl Terephthalate Moiety*” submitted by Runa Mohanta of Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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1. INTRODUCTION

Vanadium and its coordination chemistry have received a shot in the arm of recent time because of the discovery of the presence of vanadium in metalloenzymes and its medicinal and catalytic importance. The expanding knowledge of the role of vanadium in biological systems as therapeutic agents like antitumor, hypoglycaemic, antiamoebic, anticancerous agent has led to a continuously increasing interest in the coordination chemistry and solution chemistry of this element. The interaction of simple vanadium species with ligand groups bearing pharmacological activity is of growing interest. Acylhydrazones and their metal complexes have been widely studied due to their versatile applications in the fields of analytical, medicinal chemistry and biotechnology [1, 2]. Recently Avaji et al. in 2009 have reported the synthesis of macrocyclic terephthalic acid hydrazone and its corresponding metal complexes (Cu(II), Ni(II), Co(II)). These complexes found to shows promising antimicrobial activity against *A. niger*, *Penicillium* and *C. albicans* [3]. Also Maurya et al. in 2009 have synthesized various dinucleardioxido vanadium(V) complexes derived from 5, 5'-methylene bis (salicylaldehyde) and nicotinic acid hydrazide or isonicotinic acid hydrazide. These species are found to show Antiamoebic activity and are more active than the standard drug metronidazole [4].

In this dissertation I have reported the synthesis, full characterization and expected structure of two new binuclear hexadentate ligands of terephthalohydrazones (DMTHO and DMTHS) and its corresponding oxo-vanadium(V) complexes. All the synthesized ligands and corresponding metal complexes have been characterized by various spectroscopic techniques. The X-ray studies of the synthesized vanadium complexes are under process.

2. EXPERIMENTAL

2.1. Synthesis of the ligands:

The synthesis of the ligands consists of two steps.

Step-1: Synthesis of hydrazide:

The teraphthalohydrazides is prepared following a reported procedure [5] which is shown diagrammatically below (Figure 2.1).

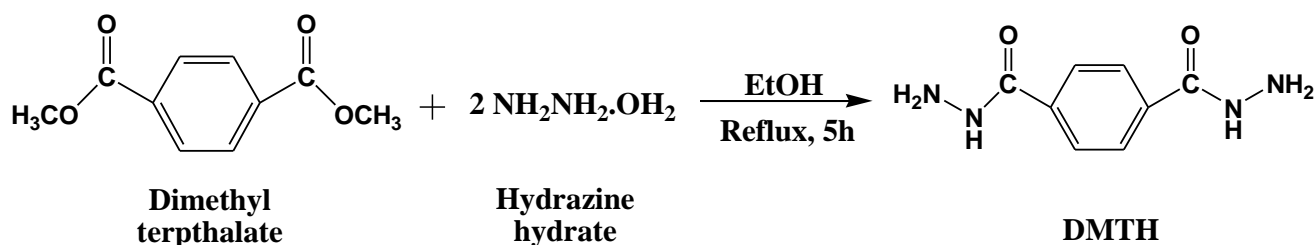


Figure 2.1 Schematic diagram for the synthesis of hydrazide

Step-2: Synthesis of Schiff's base ligands

The Schiff's base ligands used in this study were prepared by known methods which are schematically shown below:

2.1.1. Synthesis of Ligand-1 (DMTHO)

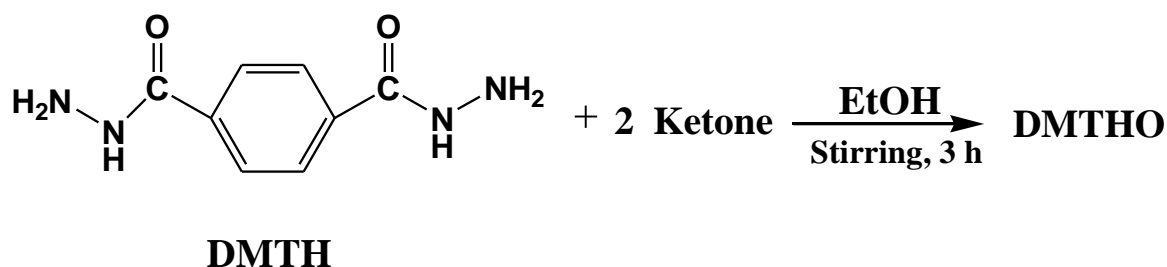


Figure 2.2 Schematic diagram for the synthesis of DMTHO

Yield =70%; M. F: $C_{24}H_{22}O_4N_4$; CHN values: Found (calc. for $C_{24}H_{22}O_4N_4$); C: 66.53 (66.97); H: 5.04 (5.11); N: 12.95 (12.02).

2.1.2. Synthesis of Ligand-2 (DMTHS)

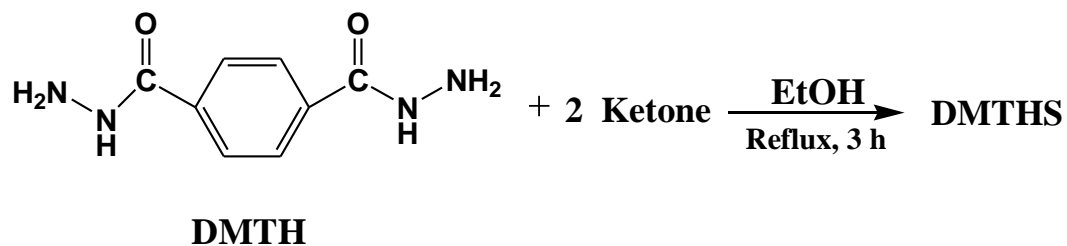


Figure 2.3 Schematic diagram for the synthesis of DMTHS

Yield =78%; M. F: $C_{22}H_{18}O_4N_4$; CHN values: Found (calc. for $C_{22}H_{18}O_4N_4$); C: 65.43 (65.67); H: 5.08 (5.11); N: 12.98 (13.02).

2.2. Synthesis of the Metal complexes:

2.2.1. Complex- 1, [DMTHSV]

Complex 1 was prepared by the following method which is given below.

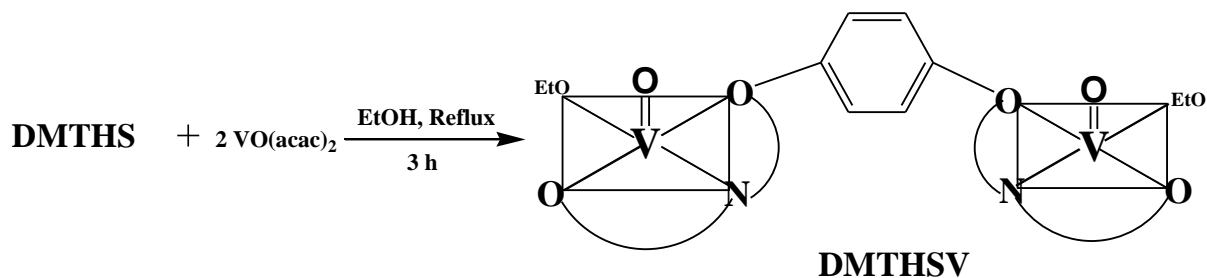


Figure 2.4 Schematic diagram for the synthesis of Complex 1 (DMTHSV).

2.2.2. Complex- 2, [DMTHOV]

Complex 2 was prepared by the following method which is given below

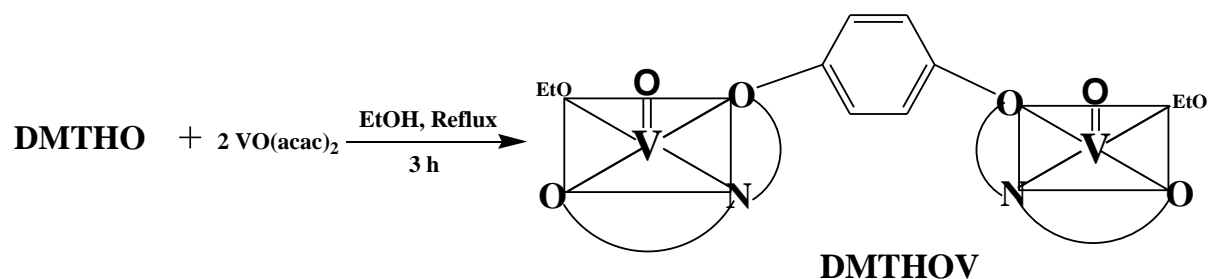


Figure 2.5 Schematic diagram for the synthesis of Complex 2 (DMTHOV).

3. RESULTS AND DISCUSSION:

Spectral characteristics:

3.1. IR Spectra of complex 1 [DMTHSV]:

The IR spectra of the ligands show stretching vibration bands of N–H, O–H and C=O at 3221, 3430 and 1661 cm^{-1} respectively. The C=N stretching vibration is found at 1626 cm^{-1} . The stretching band for C=O may be merged with that of C=N, due to which we are getting a broad band in the range of 1660-1630 cm^{-1} . In the IR spectra of complex 1 these characteristic bands are absent. The disappearance of $\nu\text{O–H}$ shows the deprotonation of the –OH group and its subsequent coordination to the central metal atom. The disappearance of $\nu\text{C=O}$ unambiguously confirms that the ligand coordinates with the vanadium in the enol form. Also the $\nu\text{C=N}$ band of the ligands at 1626 cm^{-1} has shifted to 1603 cm^{-1} in the spectra of the complexes, suggesting the coordination of the imine nitrogen to the vanadium moiety [6, 7, 8]. Appearance of peak at 990 cm^{-1} confirms the presence of V=O.

3.2. Electronic Spectra of complex 1 [DMTHSV]:

The electronic spectra of the ligand as well as complex were taken in DMSO. In the spectra of the ligand, two bands at 338 and 293 nm are present, which are assignable to intraligand transitions. In complex 1, an extra band at 420 nm was obtained which is due to ligand to metal [L-V($d\pi$), LMCT] charge transfer.

3.3. NMR Spectra of (DMTHS):

In the ^1H NMR spectra of the free ligand, the single resonance of the proton ($-\text{OH}$) is observed at 12.26, ($-\text{NH}$) at 11.21, ($=\text{CH}-$) at 8.68 and ($\text{Ar}-\text{H}$) in the region 8-6 ppm, respectively. This data suggests the formation of the ligand. The conclusion was also supported by the results of ^{13}C NMR spectra which give 22 distinct peaks as expected of the free ligand.

3.4. IR Spectra of complex 2 [DMTHOV]:

The IR spectra of the ligand, stretching vibration bands of O-H, N-H, C=O and C=N at 3408, 3245, 1670 and 1645 cm^{-1} , respectively are present. Which suggests that the formation of the ligand. However in the spectrum of complex 2 these bands were disappeared. The disappearance of O-H, N-H, C=O vibrational bands unambiguously confirms that the ligand coordinates with the vanadium in the enol form. Also the $\nu\text{C}=\text{N}$ band of the ligands at 1645 cm^{-1} has shifted to 1591 cm^{-1} in the spectra of the complexes, suggesting the coordination of the imine nitrogen to the vanadium moiety [6, 7, 8]. Also the appearance of new band at 990 cm^{-1} confirms the presence V=O group.

3.5. Electronic Spectra of complex 2 [DMTHOV]:

The electronic spectra of the ligand as well as complex were taken in DMSO. In the spectra of the ligand, appearance of two bands at 332 and 289 nm are assignable to intraligand transitions. In case of complex 2 an extra absorption band at 401 nm was obtained. This strong band at this position is due to ligand to metal [L-V(d π) LMCT] charge transfer, which indicates that metal has bound to the ligand.

5. CONCLUSION:

Two new oxovanadium(V) complexes of general formula $[V_2O_2(L)(OEt)_2]$ have been synthesized. The synthesized hydrazide, ligands, metal complexes have been characterized with the help of various spectroscopic techniques. The complexes are diamagnetic and NMR active. The electronic spectra of the complexes display several bands due to ligand to-metal charge transfer and ligand centred transitions. X-ray study of the synthesized complexes is under process.

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